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Assessment of catalytic dechlorination activity of suspended and immobilized bio-Pd NPs in different marine conditions

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ABSTRACT

Bio-palladium nanoparticles (bio-Pd NPs) are receiving extensive interests as one of the latest innovative catalysts to remove a wide variety of common environmental contaminants, such as chlorinated organic solvents. This study aims to develop a biogenic nano Pd-based remediation method for reducing chlorinated hydrocarbons from marine environments. Bio-Pd NPs were synthesized using *Shewanella oneidensis* and the catalytic feasibility of novel catalysts was evaluated by monitoring the dechlorination of TCE and Aroclor 1254 PCBs. Complete dehalogenation of TCE was achieved using bio-formed Pd-catalysts in marine conditions including: synthetic marine water, marine water slurries and marine water. Moreover, extensive dechlorination of Aroclor 1254 PCBs to mainly monochlorobiphenyls was detected excluding sediment slurries from the Venice Lagoon. Additionally, the reactivity of immobilized NPs was evaluated in marine water and sediment slurries. Our study presents a new possibility in nano-based remediation strategies toward chlorinated pollutant in marine water and sediments.

1. Introduction

Monitoring of the pollution status in the Mediterranean area has shown that this region is severely contaminated with heavy metals, oil hydrocarbons and halogenated compounds [1]. Among chlorinated hydrocarbons, trichloroethylene (TCE) and polychlorinated biphenyls (PCBs) are one of the most frequently detected organic carcinogenic pollutants in marine systems.

Different remedial strategies including physical adsorption, chemical redox reactions and biological degradation treatment have been previously developed to remove these persistent chlorinated hydrocarbons. Physical and chemical treatments are expensive, energy consuming, not environmental friendly and with slow degradation rate [2]. Furthermore, conventional bioremediation strategies rely on the use of one or more putative dechlorinating bacteria within the phylum *Chloroflexi* [3]. Although microbial-mediated reductive dechlorination of chlorinated hydrocarbons has dramatically been studied over past years, applying microbial-based dechlorination methodology for *in situ* remediation of polluted marine environments has some drawbacks: (i) working with restricted anaerobic bacteria such as *Dehalococcoides* with quite slow reaction rates [4] (ii) to complete the PCBs removal, anaerobic dechlorination of PCBs needs to be coupled with an aerobic microbial degradation pathway [5] and (iii) some chlorinated compounds are not amenable to biodegradation or the microbial activity of dechlorinating bacteria can be inhibited by the toxicity of some chlorinated hydrocarbons [6]. Therefore, more promising approaches are urgently needed to enhance environmental remediation strategies. More recently, nanoparticle-mediated remediation has become one of the leading alternatives to overcome such concerns [7]. Among metal nanoparticles, Palladium nanoparticles (Pd-NPs) have found to be an effective catalyst to remove a wide variety of common environmental contaminants, such as chlorinated organic solvents. Microbially fabricated palladium nanoparticles (bio-Pd NPs) are also considered to be an effective and promising bio-based catalyst in removing a wide variety of common environmental contaminants, such as dechlorination of chlorinated organics [8].

Reductive remediation of different chlorinated organic solvents mediated by bio-Pd NPs in groundwater system and soil have been extensively studied over the last decades. In our recent study, we evaluated the catalytic feasibility of bio-formed Pd NPs in a synthetic marine water by monitoring the dechlorination of TCE [9].

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So far, the reactivity of bio-Pd towards halogenated compounds in real marine water and sediments has not been assessed. Hence, this study aims to develop and employ biogenic nano-Pd catalysts in the remediation of chlorinated hydrocarbons deposited in the sediment and water of the Venice Lagoon and sediment from the Westerschelde, harbor of Antwerp.

Addition of metal catalysts including Pd-NPs, to marine environments can be an environmental concern. Development of immobilized recoverable catalysts in eco-compatible polymers is considered to be a promising method to overcome both environmental and economic concerns [10]. In this study, the stability and reductive dechlorination potential of bio-formed Pd-NPs towards PCBs and TCE in marine water and sediments were investigated. Finally, immobilized bioPd-NPs were employed to remove TCE from marine water and marine sediment slurries.

2. Experimental

2.1. Chemicals

Aroclor 1254 PCBs and octachloronaphtalene (OCN) were obtained from Ultra-Scientific (North Kingstown, RI, USA). Hexane and acetone (both for pesticide analysis) and Trichloroethylene (TCE) were supplied by Sigma–Aldrich (Seelze, Germany).

2.2. Preparation of bio-Pd NPs and immobilized bio-Pd NPs

Preparation of bio-Pd NPs by *Shewanella oneidensis* was performed according to De Windt et al. [6]. For immobilizing NPs, bio-Pd NPs were harvested by centrifugation (4920 × *g* for 10 min) and washed twice with ethanol. The washed bio-Pd NPs were suspended in *N*,*N*-dimethylformamide (DMF) in order to obtain 5 g L^{-1}. Afterwards, polyvinylidene difluoride (PVDF, Arkema, France) was slowly added to the solution at a final concentration of 10% wt. Subsequently, the solutions were cast on a non-woven support (Novatex FO 2471, Freudenberg, Germany) by means of an automatic film applicator. The cast speed and wet film thickness amounted to 1.2 m min^{-1} and 250 mm. Solvents were allowed to evaporate for 30 s; thereafter, the nascent film was immersed in deionized H_2O at room temperature to induce solidification (immersion–precipitation) [11].

2.3. Evaluation of catalytic TCE-dechlorination activity of bio-Pd NPs in synthetic marine water, marine water and marine sediment slurries

Batch experiments were conducted to investigate TCE dechlorination activity by NPs in different marine conditions including: synthetic marine water (26 g L^{-1} Synthetic sea salt, Instant Ocean, France), marine sandy sediment collected from the Westerschelde from the harbor of Antwerp, Belgium (Sediment A), marine water and marine sediment collected from the first industrial area Porto Marghera, Venice lagoon, Italy (Sediment B). Serum bottles (30 ml) were filled with 50 mg L^{-1} of bio-Pd re-suspended on either sterile synthetic marine water or marine water. To activate the nanocatalysts in an anaerobic bio-Pd suspension, 100% v/v of headspace was replaced with hydrogen gas after repeated cycles of N_2 overpressure and vacuum. TCE degradation was initiated by spiking 20 mg L^{-1} of TCE (Sigma–Aldrich). To monitor the catalytic activity of bio-Pd in the two types of marine sediment, 50 mg L^{-1} of bio-Pd were suspended in marine water containing 20% (dry w/v) sediment A or B. Afterwards, 100% v/v of headspace was replaced with hydrogen gas after repeated cycles of N_2 overpressure and vacuum. Using a gas-tight Hamilton syringe, all batches were spiked with TCE at a final concentration of 20 mg L^{-1}.

In all experiments, the following controls were included: (1) inactive bio-Pd (no hydrogen gas added) and (2) Pd-free control containing brackish sterile water with added H_2. All experiments were performed in triplicate [9].

2.4. Evaluation of the catalytic PCBs dechlorination activity of bio-Pd NPs in marine water and marine sediment slurries

A time series of sacrificial batch experiments were conducted to test the dechlorination activity of bio-Pd NPs towards the commercial mixture of PCBs Aroclor 1254 under different marine conditions including marine water and slurries of marine sediment A and B suspended in marine water. Experiments on marine water were performed in 15 mL serum bottles filled with 50 mg L^{-1} of bio-Pd NPs suspended in 5 ml of sterile marine water. 100% v/v of the headspace was replaced with hydrogen gas after repeated cycles of N_2 overpressure and vacuum, followed by spiking with 100 μL of an Aroclor 1254 stock solution in methanol (100 mg L^{-1} of PCBs) to obtain a final concentration of 2 mg PCBs L^{-1}. Experiments on sediment slurries were carried out in 25 mL serum bottles containing 5 mL of a 20% (dry w/v) sediment suspension in marine water amended with bio-Pd NPs at the final concentration of 50 mg (kg dry sediment)$^{-1}$. 100% v/v of the headspace was replaced with hydrogen gas after repeated cycles of N_2 overpressure and vacuum. Bottles were then spiked with 500 μL of an Aroclor 1254 stock solution in methanol (100 mg L^{-1} of PCBs) to obtain a final PCB concentration of 50 mg (kg dry sediment)$^{-1}$. Bio-Pd free controls with added H_2 were set up under all conditions tested. Bottles were incubated for 48 h at 28 °C with mild shaking (120 rpm). Two bottles of the marine water set were sacrificed after 0, 1, 3 and 8 h of incubation and two bottles of the sediment slurry sets after 0, 1, 3, 8, 24, 48 and 72 h of incubation to extract and analyze Aroclor 1254 PCBs.

2.5. Evaluation of catalytic dechlorination activity of immobilized bio-Pd NPs in synthetic marine water and marine sandy sediment slurries

The catalytic dechlorination activity of immobilized bio-Pd catalysts in PVDF membranes was evaluated by monitoring the degradation rate of TCE in the batch experiment, both in synthetic marine water and marine sediment suspension. On each batch, a total membrane surface area of 40 cm^2 of immobilized Bio-Pd catalysts in PVDF membrane were immersed in 50 ml of marine water. Catalytic activity of immobilized bio-Pd catalysts in PVDF membrane was also monitored in the 50 ml marine water containing 20% (dry w/v) of clean sandy marine sediment A. To activate the immobilized nanocatalysts in the membrane, 100% v/v of the headspace was replaced with hydrogen gas, after repeated cycles of N_2 overpressure and vacuum. Dechlorination activity of immobilized bio-Pd catalysts, upon spiking with 20 mg L^{-1} of TCE was monitored in all batches using GC–FID.

2.6. Analytical methods

TCE degradation was monitored in the headspace of samples using a GC (CP-3800, Varian, Palo Alto, CA) equipped with a flame ionization detector (FID) with the following program: injection temperature = 200 °C; detector temperature = 250 °C; initial column temperature = 35 °C (hold 2 min), increase to 75 °C at a rate of 5 °C min^{-1}; column pressure = 153 kPa (hold 2 min), increase to 176.5 kPa at a rate of 3 kPa min^{-1}. The column used was a Factor Four TM low bleed capillary column (VF-624 ms, 30 m × 0.25 mm ID [inner diameter], DF [film thickness] = 0.25 μm, Varian). The detection limit was 0.761 μM (100 μg L^{-1}).

Table 1
Physico-chemical characteristics of collected marine sediments from two sampling sites; (site A) harbor of Antwerp, (Belgium) and (site B) Venice Lagoon (Italy).

Samples	T (°C)	pH	Total organic carbon (gC Kg^{-1} dry sediment)	Sulfide (mg L^{-1})	Chlorides (gCl Kg^{-1} dry sediment)
Sediment A: harbor of Antwerp, (Belgium)	15 ± 1	7.24	0.36 ± 0.02	0.09	1.86 ± 1.33
Sediment B: Venice Lagoon (Italy)	26 ± 1	7.6	1.64 ± 0.05	13.8	7.04 ± 0.11
Marine water Venice Lagoon (Italy)	26 ± 1	7.01	–	1.76	–

PCBs degradation was monitored using solvent batch extraction methodology followed by GC-ECD analysis on two sacrificial bottles at each sampling time. Extraction from marine water samples was performed with one volume of hexane:acetone (9:1) in the presence of 1 mg L^{-1} Octachloronaphthalene (OCN) by vortexing at maximum speed for 2 min, followed by phase separation and recovery of the organic solvent. Extraction from sediment slurry samples was performed overnight at 28 °C under shaking (120 rpm) with three volumes of hexane:acetone (9:1) in the presence of 1 mg L^{-1} OCN and 0.5 volumes of elemental mercury. Organic phase was recovered after centrifugation at 2000 rpm for 10 min and freezing at −20 °C. Qualitative and quantitative analysis of the extracted PCBs was carried out using a gas chromatograph (6890 N) equipped with a HP-5 capillary column, a 63Ni electron capture detector and a 6890 series II automatic sampler (Agilent Technologies, Palo Alto, CA, USA) as described in [12]. Qualitative analysis of spiked PCBs and their possible dechlorination products was performed by comparing the retention time (relative to OCN) of the CG peaks obtained from the analysis of the sediment organic extracts with those of PCBs occurring in standard Aroclor 1242 and Aroclor 1254 and of lower chlorinated PCB pure congeners not occurring in these mixtures analysed under identical conditions. PCBs of Aroclors 1254 and 1242, injected in the presence of OCN, were identified by matching the detected peaks with the chromatographic profiles of the same standard PCB mixtures previously characterized. Quantitative analysis of PCBs was performed by using the GC-ECD response factor of each target PCB obtained through 5-points linear calibration curves of Aroclors in the range 0.5–50 mgL^{-1}. The GC-ECD response factor of each target PCB was calculated using the weight percent distribution of each congener in the same PCB standard mixtures as previously described [12]. Biphenyl concentration was determined with a gas chromatograph equipped with a HP-5 capillary column (30 m × 0.32 mm) and a FID detector under the following analytical conditions: initial temperature 60 °C; isothermal for 1 min; first temperature rate 15 °C/min; final temperature 180 °C; isothermal for 2 min; second temperature rate 10 °C/min; final temperature 275 °C; isothermal for 9 min; injector (split mode) 280 °C; split ration 18.7:1; FID 250 °C; H_2 flow 40 ml/min, Air flow 450 ml/min; carrier gas flow (nitrogen) 60 ml/min; sample volume 1 μl.

3. Results and discussion

3.1. Sediment characteristics

NPs-mediated remediation has been highlighted as a next generation of environmental remediation technologies in removing a wide variety of common environmental contaminants [7]. Earlier studies showed that palladium decorated bacterial cells (bio-Pd) of *S. oneidensis* were actively able to dechlorinate PCBs and Cl-solvents in fresh water systems [6,8]. Recently, we demonstrated that the bio-formed Pd-NP using marine indigenous bacteria were still active in synthetic marine conditions in removing TCE [13]. So far, catalytic activity of bio-formed Pd NPs in real marine environments has not been explored. Therefore, assessment of catalytic dechlorination activity of Pd-NPs under environmentally benign conditions is necessary for future *in situ* application of this catalyst. For this purpose, we monitored the dechlorination activity of bio-Pd NPs in different marine conditions including: synthetic marine water, marine sandy sediment collected from the Westerschelde from the harbor of Antwerp, Belgium (Sediment A), marine water and marine sediment collected from the first industrial area Porto Marghera, Venice lagoon, Italy (Sediment B). In addition, to assess the influence of physico-chemical properties of sediment matrix on the activity of bio-Pd catalyst, dechlorination activity of this catalyst was examined in two different types of marine sediments. The physicochemical characteristics of the collected sediments from both sampling sites are shown in Table 1. The sediment from site B was a black and silty mud containing 13.8 mg L^{-1} sulfide, probably due to the microbial sulphate reduction activities. Whereas, collected sediment from site A was a sandy sediment with a remarkable lower content of sulfide (1.7 mg L^{-1}).

3.2. Reductive dehalogenation of TCE in synthetic marine water, marine water and marine sediment slurries using bio-Pd NPs

Monitoring of the pollution status in the Mediterranean area has shown these regions are severely contaminated with heavy metals, oil hydrocarbons and halogenated compounds [1]. Among chlorinated organic compounds, TCE has been detected as one of the common marine water and marine sediment contaminant. Nowadays, environmental nano-based remediation of pollutants such as TCE using biogenic nanocatalysts is receiving extensive interests. Previous studies on catalytic activity of bio-Pd NPs were mainly focused on TCE removal from freshwater [14] and synthetic marine water [9]. No information is available concerning the behavior of this nanocatalyst in real marine samples. Hence, in this study, the performance of bio-Pd NPs in dechlorination of TCE was evaluated in collected marine water from the Venice Lagoon (Italy) in compare with synthetic marine water. A removal rate of 20 mg L^{-1} h^{-1} was obtained in synthetic marine and real marine water batches using activated bio-Pd nanocatalysts with an external electron donor source. Moreover, no TCE dechlorination was detected in all control systems including inactive bio-Pd (no hydrogen gas added) and Pd-free control containing brackish sterile water with added H_2 (data not shown). As a result, bio-Pd NPs have obviously possessed an excellent reductive dechlorination activity in the aqueous environment including marine water.

In the case of sediment slurries, all spiked TCE was completely removed from marine sediment slurries of sediment A within 60 min. Conversely, no TCE degradation was detected in slurries of sediment B (Fig. 1). Monitoring the catalytic activity of bio-formed Pd-NP in two types of marine sediments revealed that the physicochemical properties of sediment can affect the activity of catalysts. The poisoning effect of sulfide ions on the activity of Pd-based catalysts is a well-known problem [15]. Previously, several studies have shown that sulfide ions can impeded the catalytic activity of Pd NPs by saturating surface of catalysts [16,17]. Deactivation of catalysts in marine sediment from the Venice Lagoon, Italy, can be attributed to the sulfide content of this site. Problematically, practical application of bio-Pd NPs in sulfide contaminated sediment cannot be achieved. Therefore, development of sulfide resistance Pd NPs needs to be investigated in further studies.

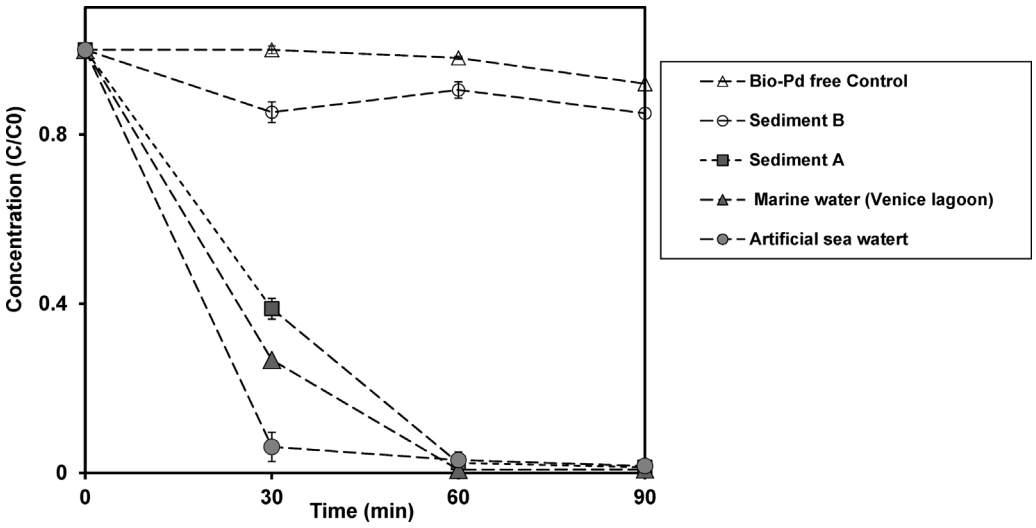

Fig. 1. Time course of TCE dechlorination in marine water, marine sediment slurries and artificial marine water using 50 mg L^{-1} bio-Pd formed by *S. oneidensis*.

3.3. Reductive dehalogenation of PCBs in marine water and marine sediment slurries using bio-Pd NPs

Among chlorinated organic compounds, PCBs has been detected as highly toxic and persistent contaminants in marine environments [18]. So far, microbial reductive dechlorination of these persistent compounds in marine water and sediments has been extensively studied [19,20]. Nevertheless, the slow rate of microbial reduction and difficulties in working with restricted anaerobic bacteria have been limited the *in situ* application of this method. However, application of nano-catalysts for dehalogenating persistent chlorinated organics such as PCBs has been considered as a pioneered methodology in remediation strategies due to the fast removal rate of this method. Few studies are available related to

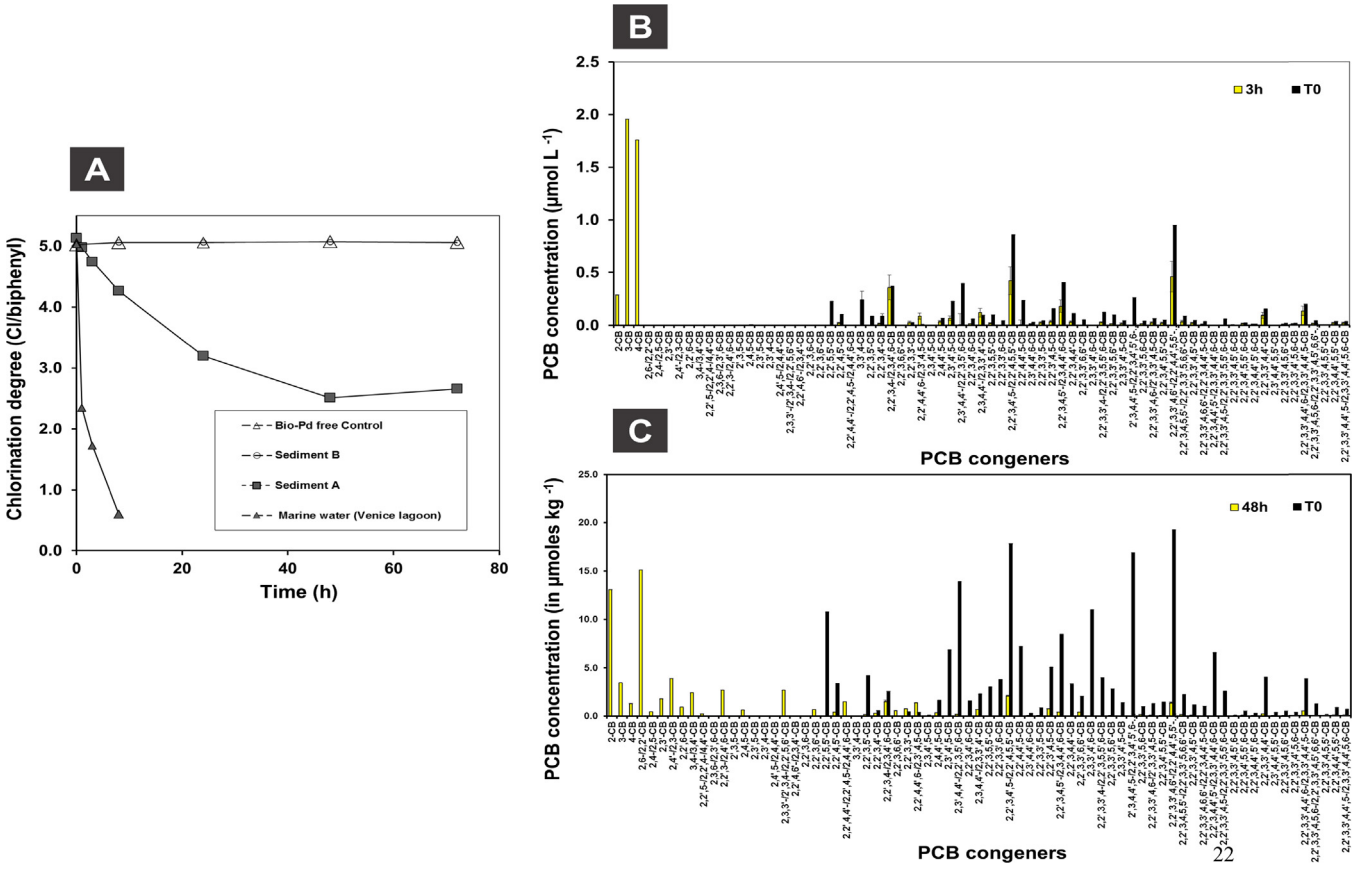

Fig. 2. A: Time course of bio-Pd mediated dechlorination of Aroclor 1254 PCBs in marine water (PCBs 2 mg L^{-1}, bio-Pd 50 mg L^{-1}) and in marine slurries of sediment A and B suspended in marine water (PCBs and bio-Pd 50 mg (kg dry sediment)$^{-1}$ each); dechlorination is represented as the decrease of the average number of chlorine atoms per biphenyl molecule, B: congener distribution of Aroclor 1254 PCBs in marine water at time 0 (black bars) and of their dechlorination products after 3 h of incubation with bio-Pd NPs (yellow bars) and C: congener distribution of Aroclor 1254 PCBs in sediment A slurries at time 0 (black bars) and of their dechlorination products after 48 h of incubation with bio-Pd NPs (yellow bars). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

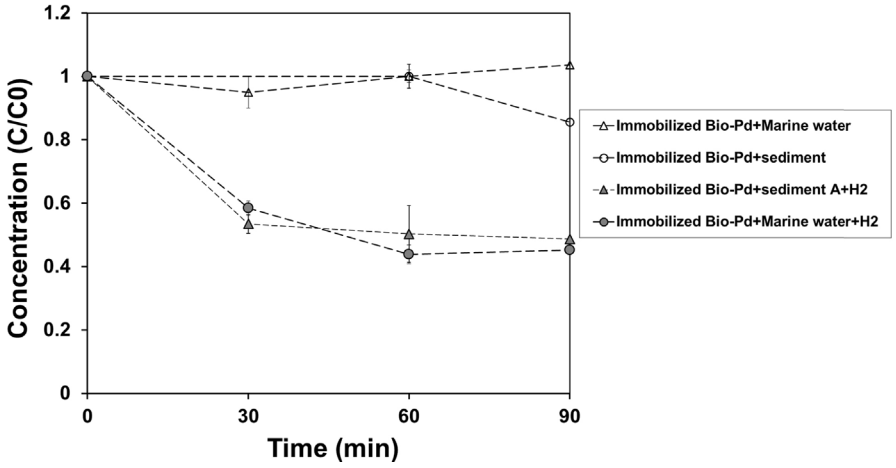

Fig. 3. Time course of TCE dechlorination (C_0 = 20 mg L^{-1}) in marine water and sediment A slurries catalyzed by immobilized bio-Pd NPs in PVDF membranes.

the application of noble catalyst in removal of PCBs in marine sediments. Bio-formed Pd-NP has also been presented a promising catalytic activity for *in situ* remediation of contaminated groundwater and fresh water [8]. So far, the catalytic feasibility and stability of this catalyst in marine conditions was not studied before.

In this study, the catalytic dechlorination activity of bio-Pd NPs was investigated towards the commercial PCB mixture Aroclor 1254 under the same marine conditions tested for TCE dechlorination, namely (i) marine water and (ii) slurries of two marine sediments suspended in marine water. No PCB dechlorination was observed in all bio Pd-free controls over 72 h of incubation (Fig. 2A). The commercial mixture of PCBs Aroclor 1254 is characterized by an average number of chlorines per biphenyl molecule of 5.1 and the lack of mono- and several di-chlorinated PCB congeners. After 3 h incubation in marine water with activated bio-Pd, Aroclor 1254 PCBs were extensively dechlorinated mainly to mono-chlorinated congeners (Fig. 2B), that represented 61 mol% of residual PCBs, and to biphenyl, that represented 33% of total molar mass. This was resulted a decrease in the average number of chlorines per biphenyl molecule from 5.1 to 2.6 (Fig. 2A). PCBs were further dechlorinated to biphenyl within the 8th hour of incubation, when 5.8 ± 2.1 μmoles of PCB/L (ca. 85% of spiked PCBs) were fully dechlorinated to biphenyl, and the average number of chlorine atoms per biphenyl molecule was decreased to less than 1.0 (Fig. 2A). So far, such a remarkable PCB dechlorination activity in terms of rate and extent has never been reported in marine conditions. Bio-Pd NPs also exhibited a remarkable catalytic activity towards Aroclor 1254 PCBs in slurries of sediment A. After 48 h of incubation, the original PCB congeners were depleted by 93% and converted into mono- and di-chlorinated congeners (Fig. 2C), that represented 28 mol% of residual PCBs. In addition, the total concentration of PCBs was decreased from 186 ± 0.5 to 64 ± 9 μmoles/kg dry sediment at the end of the incubation period, indicating that a remarkable fraction of the original PCB congeners was probably fully dechlorinated to biphenyl. However, no biphenyl was detected in the organic extracts. This was probably due to (i) the low concentration of the accumulated biphenyl (close to the detection limit), and/or (ii) to a lower biphenyl extraction yields from the sediment slurry in compare with the sediment-free system. The PCB dechlorination activity observed in sediment A slurries was remarkably slower and more limited than sediment-free marine water. This might be due to the consequence of a less intimate contact between PCBs adsorbed onto the sediment and bio-Pd NPs. To our knowledge, this is the first time that such an extensive and rapid dechlorination of a complex commercial mixture of PCBs in marine sediments has been obtained under mild, ambient conditions. In slurries of sediment B amended with bio-Pd NPs, instead, no PCB dechlorination was observed throughout incubation (Fig 2A). This clearly suggests that sediment characteristics, in particular the content of sulfide, may strongly affect the catalytic activity of bio-Pd NPs, as discussed above.

3.4. Develop a recovery alternative for bio-Pd after in situ application

One of the crucial limiting factor in the application of Pd-based nanocatlysts is their cost of production. In addition, accumulation of metallic catalysts, including Pd-NPs, in the marine environment increases environmental concerns. Hence, development of immobilized recoverable catalysts in eco-compatible polymers has been considered to be a promising method to overcome of both environmental and economic concerns.

In this study, bio-Pd NPs was immobilized in dimethylformamide (DMF) polymer supported on Novatex layer. The catalytic feasibility and stability of immobilized catalysts was evaluated by monitoring the dechlorination of TCE in marine water and sediment A. Immobilized bio-Pd NPs in PVDF membranes were tested for TCE removal from marine water and marine sediment slurries. Fig. 3 shows the TCE dechlorination rate of immobilized catalysts

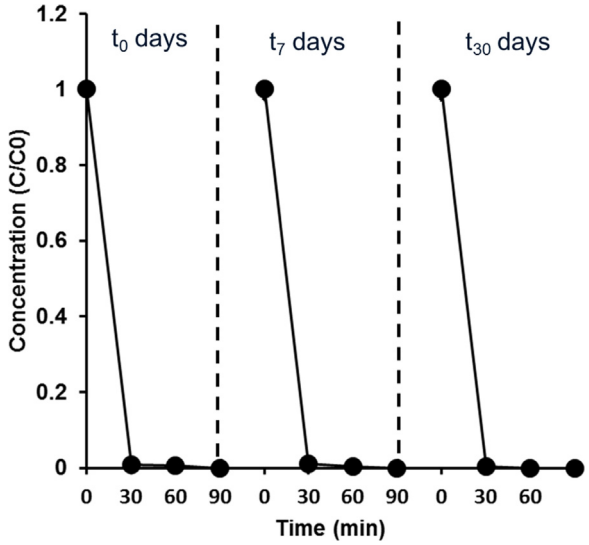

Fig. 4. Time course of TCE dechlorination (C_0 = 20 mg L^{-1}) using bio-Pd catalysts in marine water at 0, 7 days and 30 days.

in compared with suspended catalysts in marine water and marine sediment slurries. Almost 50% of TCE was dechlorinated within 90 min., using immobilized bio-Pd catalysts from marine water and marine sediment slurries. Normally, catalytic dechlorination activity of Pd NPs is taking place on the particles surface [21]. Therefore, entrapment of Pd-NPs in a polymeric matrix can be a reason for decreasing the potential of catalysts in removing TCE. In addition, accessibility of the required atomic hydrogen for activating catalysts was limited after immobilizing NPs in complex matrix. Previously, catalytic activity of chemically synthesized Pd catalysts immobilized in PVDF towards TCE dechlorination was reported by [22]. They suggested a bimetallic catalytic system for improving the catalytic activity NPs after immobilizing in a matrix. However, our results clearly indicated that the membrane-immobilized bio-Pd NPs can be a highly potential applied systems to overcome of both environmental and economic concerns after in situ application.

3.5. Stability and activity of bio-Pd in brackish water over time

Another major concern in the application of nano-based catalysts is the lifetime of catalysts. The removal rate of TCE using bio-Pd NPs was tested over several days (0, 7 and 30 days) to estimate the catalyst lifetime. The bio-Pd formed by *S. oneidensis* showed a stable dechlorination activity in removing TCE over several days. The same removal rate of 20 mg L^{-1} h^{-1} at 0, 7 and 30 days (Fig. 4) in marine water batches suggested that the catalytic activity of bio-Pd NPs during one month of experiments in marine water slurries was remained stable. Physico-chemical processes in synthesis of Pd-NPs are typically combined with a post-synthesis treatment using a surfactant or polymeric ligands, in order to improve the stability of catalysts. However, all of the readily used methods are cost effective and might be not environmentally friendly. Unlike Physico-chemical processes, in microbial synthesis of Pd-NPs the need of stabilizer and capping agent as a post-synthesis treatment is eliminated. In addition, this method is known as a bio-compatible, clean and eco-friendly methodology in developing different types of stable NPs [23].

4. Conclusion

This study demonstrates that (i) bio-Pd NPs can rapidly and extensively dechlorinate Cl-solvents and complex PCB mixtures in marine environments, and (ii) the catalytic dechlorination activity of these catalysts is affected by the physico-chemical properties of marine sediments. In addition, development of immobilized NPs in eco-compatible polymers in this study was introducing a promising strategy for future recovery option of bio-Pd NPs after *in situ* application. In conclusion, the use of biogenic NPs represents a promising approach for future marine nano-based remediation applications and green procedure to fabricating of NPs for long term use in aqueous media.

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